

APPLICATION OF AN ATOMIC OXYGEN BEAM FACILITY
TO THE INVESTIGATION OF SHUTTLE GLOW CHEMISTRY

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Abstract. A facility for the investigation of the interactions of energetic atomic oxygen with solids is described. The facility is comprised of a four-chambered, differentially pumped molecular beam apparatus which can be equipped with one of a variety of sources of atomic oxygen. The primary source is a DC arc-heated supersonic nozzle source which produces a flux of atomic oxygen in excess of $10^{15} \text{ cm}^{-2} \text{ sec}^{-1}$ at the target, at a velocity of 3.5 km sec^{-1} . Results of applications of this facility to the study of the reactions of atomic oxygen with carbon and polyimide films are briefly reviewed and compared to data obtained on various flights of the space shuttle. A brief discussion of possible application of this facility to investigation of chemical reactions which might contribute to atmosphere-induced vehicle glow is presented.

Introduction

A spacecraft in the altitude range of 200–700 km experiences bombardment by an atmosphere whose primary constituent is neutral atomic oxygen [Hedin et al., 1977]. Although the ambient gas temperature is only on the order of 1000 K, the 8 km sec^{-1} velocity of the spacecraft causes the oxygen atoms to strike satellite surfaces at a relative kinetic energy of 500 kJ mole^{-1} (5 eV). At shuttle altitudes, the atomic oxygen density is on the order of 10^9 cm^{-3} , which corresponds to a flux of about $10^{15} \text{ cm}^{-2} \text{ sec}^{-1}$. These conditions present a regime of gas-surface chemistry which has been the subject of very little experimental investigation because of the difficulties inherent in reproducing them in the laboratory. A variety of effects observed on NASA and USAF spacecraft have been ascribed to the action of the ambient atmosphere. These include material erosion [Leger et al., 1983, 1984], optics degradation [Arnold et al., 1982], and luminescence [Banks et al., 1983; Yee and Abreu, 1983].

This paper describes a facility assembled specifically for the investigation of the interactions of energetic atomic oxygen with solid surfaces. The major elements of this facility, which are described below, are the four-chambered, differentially pumped molecular beam apparatus, the provisions for mounting and interrogating solid samples, and the DC arc-heated supersonic atomic beam source. Results of experimental work using this facility which demonstrate its utility in

performing its appointed task are briefly presented along with a brief assessment of the potential for application of this facility to investigation of chemistry which may contribute to vehicle glow.

Facility Description

Vacuum System

Figure 1 shows a schematic representation of the molecular beam apparatus. The vacuum system is comprised of four differentially pumped stainless steel chambers. The first three chambers are 0.46 m^3 boxes equipped with Viton or Buna-N "O-ring" seals. Each is pumped by an oil diffusion pump. The pumps on the second and third chambers are equipped with gate valves and liquid nitrogen cooled baffles.

The fourth chamber is a cylindrical clean chamber utilizing crushed metal seals. It is recessed into chamber 3 to reduce the total length of the facility (as measured from the source). This chamber is equipped with a high vacuum gate valve (Huntington model GVAP-600) and a 570 l-sec^{-1} turbomolecular pump (Balzers model TPU 510). The turbomolecular pump is used in preference to more conventional UHV pumping technology because of the large helium load which this chamber must bear.

Sample and Analysis Systems

The facility is equipped with a quadrupole mass spectrometer (Extranuclear Laboratories, Inc.) comprised of a crossed-beam electron-impact ionizer, a quadrupole mass filter with 17 mm diameter rods, and a Johnston MM-1 particle multiplier. The mass spectrometer has been used so far only for beam source characterization.

When solid samples are to be bombarded, they may be mounted either in chamber 2, when it is desirable to maximize the available beam flux on target, or in chamber 4 when sample cleanliness is the paramount concern. A liquid nitrogen cooled shroud surrounds samples in chamber 2 to inhibit contamination. The beam is typically collimated to subtend a circular spot of approximately 7 mm in diameter when samples are mounted in this shroud, however, spots as large as 17 mm are possible. A three-axis-plus-rotation precision manipulator is provided for mounting solid samples. Active temperature control on the range of 300-450 K is typical.

The only in situ diagnostics currently available in this facility are optical. Transmission measurements of samples mounted in either location are possible. Figure 2 shows a schematic representation of the optical path for transmission measurements in chamber 4. Ultraviolet transmission has been used to measure the rate of oxidation of carbon by high velocity atomic oxygen [Arnold and Peplinski, 1984a] and infrared transmission has been used to measure the effect of atomic oxygen on clean and contaminated infrared optics [Arnold et al., 1982].

Atomic Oxygen Sources

The primary beam source used in this facility is a DC arc-heated supersonic nozzle source which relies on a modified, commercially available plasma torch. The beam source has been described in detail elsewhere [Silver et al., 1982; Arnold and Peplinski, 1984b]. Typical beam source operating conditions and performance specifications are summarized in Table 1.

Two other beam sources for producing atomic oxygen are available for use in this facility: a microwave discharge source [Arnold et al., 1982] and a resistively-heated thermal dissociation source [Henderson et al., 1969] for which iridium or rhenium source tubes with a variety of orifice diameters are available. Both sources are capable of producing substantial fluxes of atomic oxygen, but with velocities on the order of 1 km sec^{-1} . These lower velocity sources are needed to gain a more complete understanding of the kinetics of the reactions of atomic oxygen with solids.

All three of the sources produce light as well as atomic beams. This light presents a potential interference to experiments aimed at measuring luminescence. In the case of the microwave discharge source, this problem can be circumvented by introducing a bend in the source between the discharge region and the nozzle. For the other two sources this is not possible.

Since the beam from either the DC arc source or the thermal dissociation source is comprised of neutral atoms and molecules, separation of the beam from the light can only be readily effected by a mechanical chopper. A two-segment slotted-disk velocity selector of 40% nominal transparency has been designed for this facility [Fluendy and Lawley, 1973]. The role of this device is not to prepare a beam of narrow velocity distribution, but merely to block species, such as photons, traveling at velocities in excess of the selected velocity. Since the selector has only two disks, it naturally has an infinite number of low-velocity side bands. This device has not heretofore been used for experiments performed in this facility.

Facility Applications

Reaction of Atomic Oxygen with Solids

This facility has been used to investigate the rate of reaction of atomic oxygen with two types of carbon [Arnold and Peplinski, 1984a, 1985a] and with Kapton film, a polyimide material manufactured by E.I. du Pont de Nemours & Co., Inc. [Arnold and Peplinski, 1985b]. The results of these investigations are summarized very briefly below.

Carbon. Figure 3 shows an Arrhenius plot (in carbon surface temperature) of the probability of reaction of atomic oxygen with carbon including data from ground-based measurements and flight experiments and other observations from various flights of the space shuttle. The reaction probability plotted is defined as the probability that an oxygen atom impact will remove a carbon atom from the surface,

regardless of its final state of aggregation. (For a detailed discussion of these data the reader should consult [Arnold and Peplinski, 1984a] and works cited therein.)

The open circles and open triangle represent the results of measurements performed in this facility. The dashed line labeled "Park" is a fit to several laboratory measurements of the rate of reaction of atomic oxygen with various forms of carbon, under more or less thermal conditions [Park, 1976]. The other data include limits on the reaction probability inferred [Arnold and Peplinski, 1984a] from removal of carbon surfaces on the STS-3 Plasma Diagnostics Package (G.B. Murphy, University of Iowa, Department of Physics and Astronomy, Iowa City, IA, private communication, 1982) and on the STS-4 Marshall Space Flight Center's Induced Environment Contamination Monitor Passive Sample Array [Peters et al., 1983], a probability calculated from the observed thickness loss of vitreous carbon included on the STS-5 Evaluation of Oxygen Interaction with Materials (EOIM) passive sample array [Arnold and Peplinski, 1985a], and the reaction probability calculated from the observed rate of mass loss from an amorphous carbon-coated temperature-controlled quartz crystal microbalance on the Goddard Space Flight Center's Contamination Monitor Package flown as a "Get-Away Special" on STS-8 (J.J. Triolo, NASA/Goddard Space Flight Center, Greenbelt, MD, private communication, 1984).

These data lead one to the conclusion that the rate of reaction of atomic oxygen with carbon, at collision energies of up to 100 kJ mole^{-1} (1 eV), does not depend strongly on the translational energy of impact. Indeed when one compares laboratory and flight data for similar samples of carbon, the evidence that rates occurring on-orbit are significantly different from the thermal rate of reaction of O atoms with carbon is not strong. However, the results of Gregory and Peters (not shown on Figure 4), who infer probabilities in excess of 0.1 from STS-8 EOIM results, militate against drawing an unambiguous conclusion in this matter (J. C. Gregory, Chemistry Department, the University of Alabama at Huntsville, private communication, 1985).

Kapton. Table 2 shows a comparison between the average probabilities for the reaction of atomic oxygen with Kapton measured in this facility [Arnold and Peplinski, 1985b] and inferred from the STS-5 and STS-8 EOIM experiments [Leger et al., 1983, 1984]. In this case, the reaction probability is conventionally defined as the thickness of material removed divided by the fluence of atomic oxygen incident on the sample.

The agreement between the laboratory and flight data is quite good in comparison to the uncertainties in the various data. This relatively good agreement suggests that there is not a great dependence on O atom impact energy of the average efficiency of the reaction of atomic oxygen with Kapton over a range of impact energy from 1 to 5 eV.

Luminescent Reactions

Several possible contributing mechanisms have been proposed to explain the vehicle glow phenomenon. These include surface catalyzed recombination of atmospheric radicals [Torr et al., 1977; Reeves, 1982],

production of excited products from oxygen reactions with materials [Slanger, 1983], recombination collisionally dissociated of nitrogen [Green, 1984], and vehicle plasma interactions [Papadopoulos, 1984].

Considering the complexity of the problem and the scarcity of unambiguous data, one cannot yet make any definitive assessment of the relative importance of these various processes in creating the observed glows. However, one can proceed reasonably to investigate these processes experimentally, with both flight and laboratory experiments. It is a valid and important point that there appears to be no way to simulate the "shuttle glow" in the laboratory. The shuttle environment is too complex and uncertain. However, simulation is not necessarily the proper function of laboratory investigations of spacecraft environmental phenomena. Rather, their role is to elucidate mechanistic details which are difficult to address in flight experiments on account of operational constraints, background interferences, scarcity of opportunities, or expense.

Visible luminescence from surface catalyzed excitation. In the earliest published reference to atmosphere-induced vehicle glow [Torr et al., 1977], it was hypothesized that recombination of adsorbed atmospheric O and NO to produce excited NO₂ in the gas phase was responsible for the observed visible emission. This explanation has subsequently been proposed repeatedly. [Reeves, 1982; Mende and Swensen, 1985].

The production of excited products by surface catalyzed radical recombination is a well-documented phenomenon [Mannella and Harteck, 1961]. However, both Mende and Swenson and Torr et al. have suggested that for the O + NO recombination luminescence to account for the majority of the observed glows, the spectrum of the NO₂ product must be shifted compared to the spectrum obtained from 3-body gas-phase recombination [Golde et al., 1973]. There is not sufficient information from experiments in which the spectrum of the product NO₂ is not perturbed by subsequent gas-phase collisions to answer whether this mechanism is important in the creation of the observed shuttle glow.

Clearly one wishes to investigate the luminescence from surface-catalyzed NO₂ production under "single collision" conditions so that one measures the spectrum of the nascent products. This suggests that molecular beam techniques be used. A schematic representation of such an experiment is shown in Figure 4.

One may estimate the signal from such an experiment as follows. The number density of NO₂^{*} product near a surface on which O and NO are recombining may be formally expressed as

$$[\text{NO}_2^*] \cong k_1 F_0 [\text{NO}_{\text{ads}}]/v_1 + k_2 F_{\text{NO}} [\text{O}_{\text{ads}}]/v_2 + k_3 [\text{O}_{\text{ads}}][\text{NO}_{\text{ads}}]/v_3 \quad (1)$$

where three different processes are considered to be operational:

1. Reaction of an incident O atom with an adsorbed NO molecule;

2. Reaction of an incident NO molecule with an adsorbed O atom;
3. Reaction of an adsorbed O atom with an adsorbed NO molecule.

In equation (1) the rate coefficients k_1 and k_2 have units of area (reaction cross-section) and k_3 has units of area/time (like a diffusion coefficient). The quantities v_i are the average velocities with which the product is ejected as a result of each of the three formation processes.

In practice, to make a rough estimate of the photon emission rate from such an experiment, one approximates equation (1) by assuming that the NO_2 production rate will be limited by one or the other of the reagent fluxes. Therefore one obtains

$$[\text{NO}_2^*] \approx p F_1 / \langle v \rangle \quad (2)$$

where F_1 is the limiting flux, p is some effective probability, and $\langle v \rangle$ is an average velocity of the product.

If one approximates the volume emission rate as $[\text{NO}_2^*]$ divided by the average radiative lifetime, τ_{rad} , and assumes collection with $f/1$ optics from an 0.5 cm^3 volume, then the rate at which photons fall on the detector per unit wavelength, S , is given by

$$S \approx \frac{p F_1}{10 \langle v \rangle \tau_{\text{rad}} \Delta \lambda} \quad (3)$$

If one presumes that it is the O atom flux that limits the reaction rate, then one needs to invoke a value of about 10^{-7} for p to rationalize the orbital observations. In this facility O atom fluxes on the range of 10^{14} - $10^{15} \text{ cm}^{-2} \text{ sec}^{-1}$ are easily realized. The product $\langle v \rangle \tau_{\text{rad}}$ can be expected to range from 3-20 cm. The bandwidth, $\Delta \lambda$, is expected to be approximately 3000 \AA . Thus total photon arrival rates range from 10-1000 photon/ \AA/sec . Using cooled, a red-sensitive photomultiplier tube, with photon counting detection, measurement of a moderately well resolved spectrum at these signal levels should be possible.

Infrared Luminescence

The observation of moderately intense luminescence in the visible near spacecraft surfaces naturally raises the question of whether there is also a significant infrared component associated with the glow. At least one of the proposed mechanisms for glow production suggests such to be the case [Slanger, 1983]. Observation of the shuttle from the ground suggests that there may be more near infrared emission from the shuttle than can be explained by thermal emission or scattering from other sources (F. Witteborn, NASA/Ames Research Center, private communication, 1985).

The long lifetimes associated with infrared emission render the laboratory investigation of infrared luminescence under "single collision conditions" difficult. Excited molecules tend to leave the

detector field-of-view or to strike chamber walls in times much less than their radiative lifetimes. However, the technology for direct, laser-induced fluorescence (LIF) measurement of internal state distributions of reaction products, from which one may readily calculate net emission spectra, is well established [Kinsey, 1977]. Recently this technology has begun to find application in gas-surface scattering research [Cardillo, 1985].

Because of the wide use of carbon, carbon-filled, and carbon-containing materials on spacecraft surfaces, the internal state distribution of the CO product of the $O + C_s$ reaction is of interest. Since LIF is a number density detector, one again needs to estimate the number density or "effective pressure" of products to ascertain whether a measurement is feasible. This number density is given by

$$[CO] \cong pF_0/v_{CO} \quad (4)$$

where p is the reaction probability, F_0 is the flux of atomic oxygen, and v_{CO} is the product velocity. For a reaction probability of 0.01, a flux of $4 \times 10^{14} \text{ cm}^2 \text{ sec}^{-1}$, and a thermal product velocity, one estimates the CO number density to be approximately $8 \times 10^7 \text{ cm}^{-3}$, which is roughly equivalent to a pressure at room temperature of 3×10^{-9} Torr.

Detection of CO internal state distributions by LIF can be accomplished by excitation of the A-X transition at approximately 148 nm. Hepburn has reviewed the technology for coherent VUV generation for this application [Hepburn, 1984]. He estimates the detection limit for CO (at 300 K) to be 10^{-10} Torr. Thus, by the application of established technology, a useful experiment to assess the potential for non-thermal infrared luminescence from vehicles in LEO is feasible.

Summary

A facility which has proven to be useful in the investigation of oxygen atom interaction with materials has been described. Order-of-magnitude estimates of signal strengths suggest that this facility will be useful in the investigation of surface-catalyzed excitation reactions and of energy disposal in gas-solid reactions which produce volatile products. Both of these processes have been suggested as contributors to the "shuttle glow."

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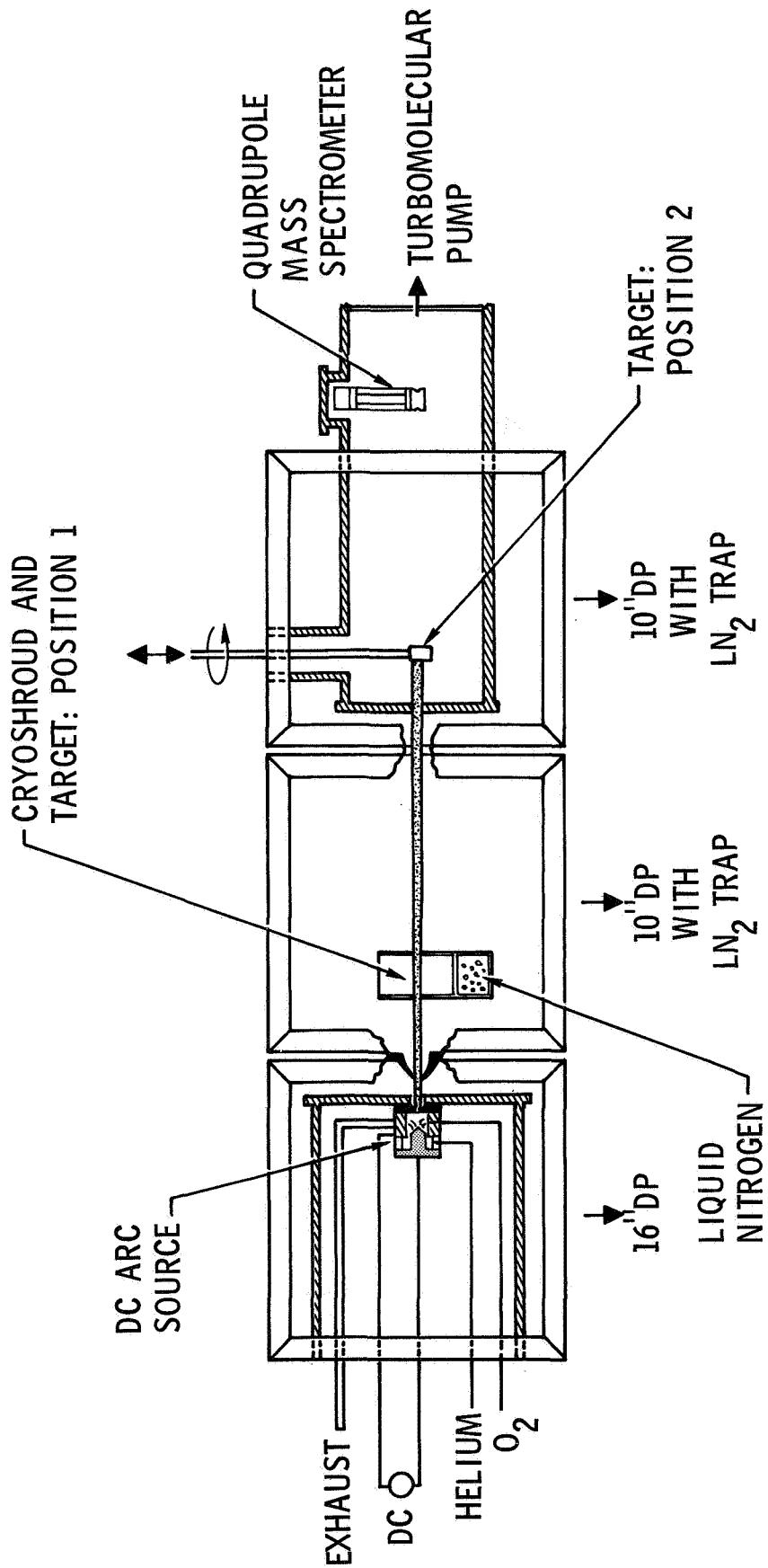


Fig. 1. Schematic representation of the atomic oxygen beam facility.

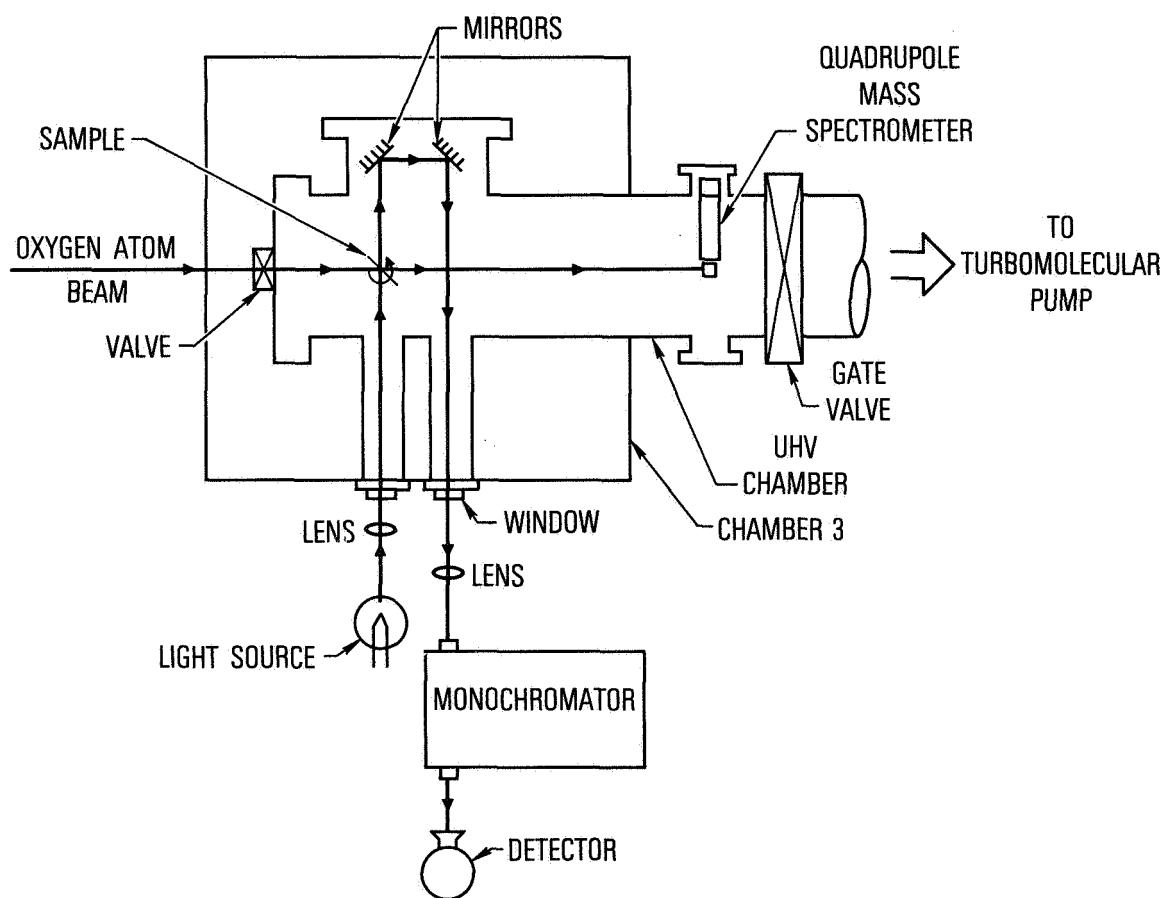


Fig. 2. Schematic representation of the fourth (clean) chamber showing path for in situ optical transmission measurements.

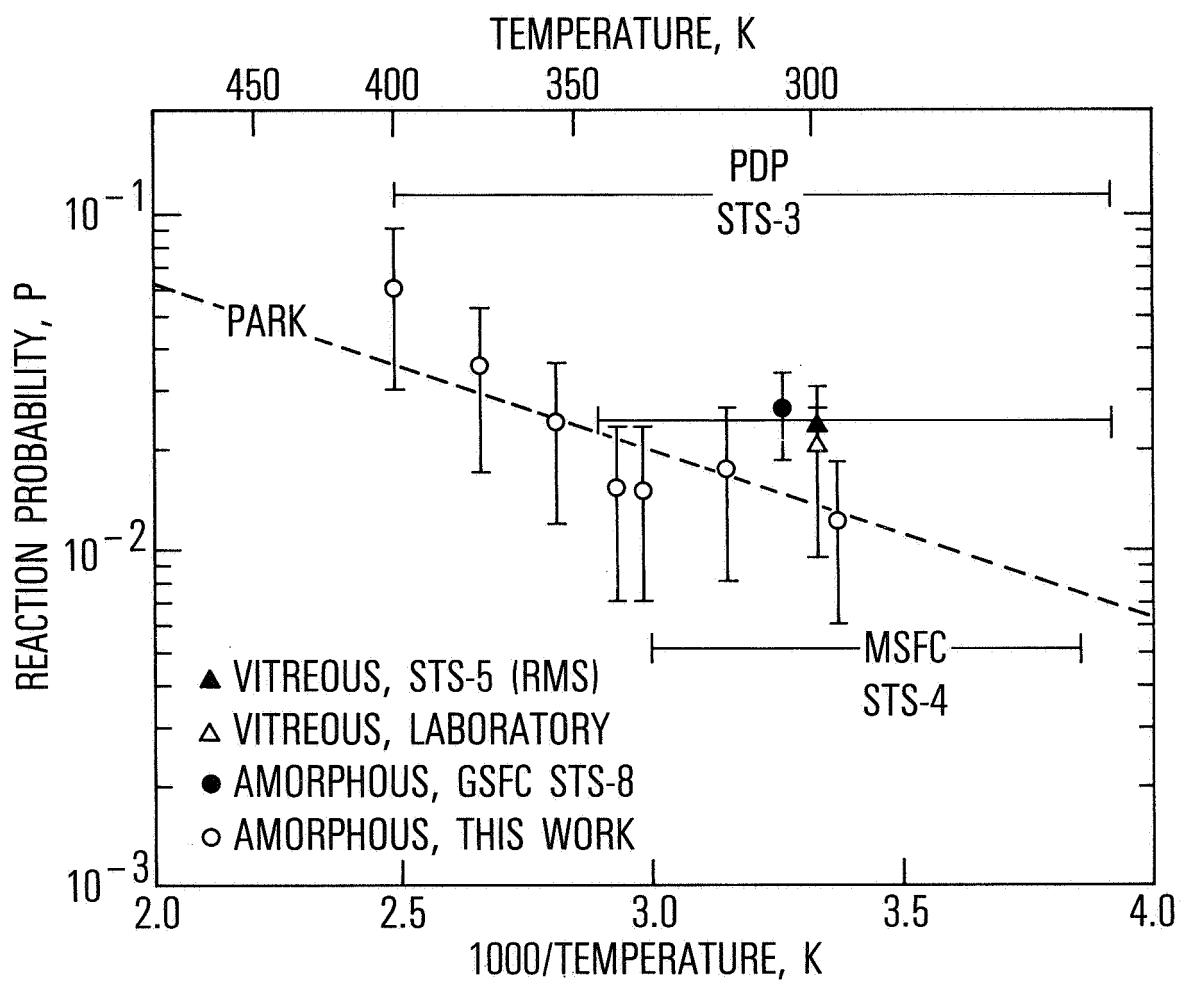


Fig. 3 Arrhenius plot (in carbon surface temperature) of the probability of the reaction of atomic oxygen with carbon. Various laboratory and flight data are shown. (See text.)

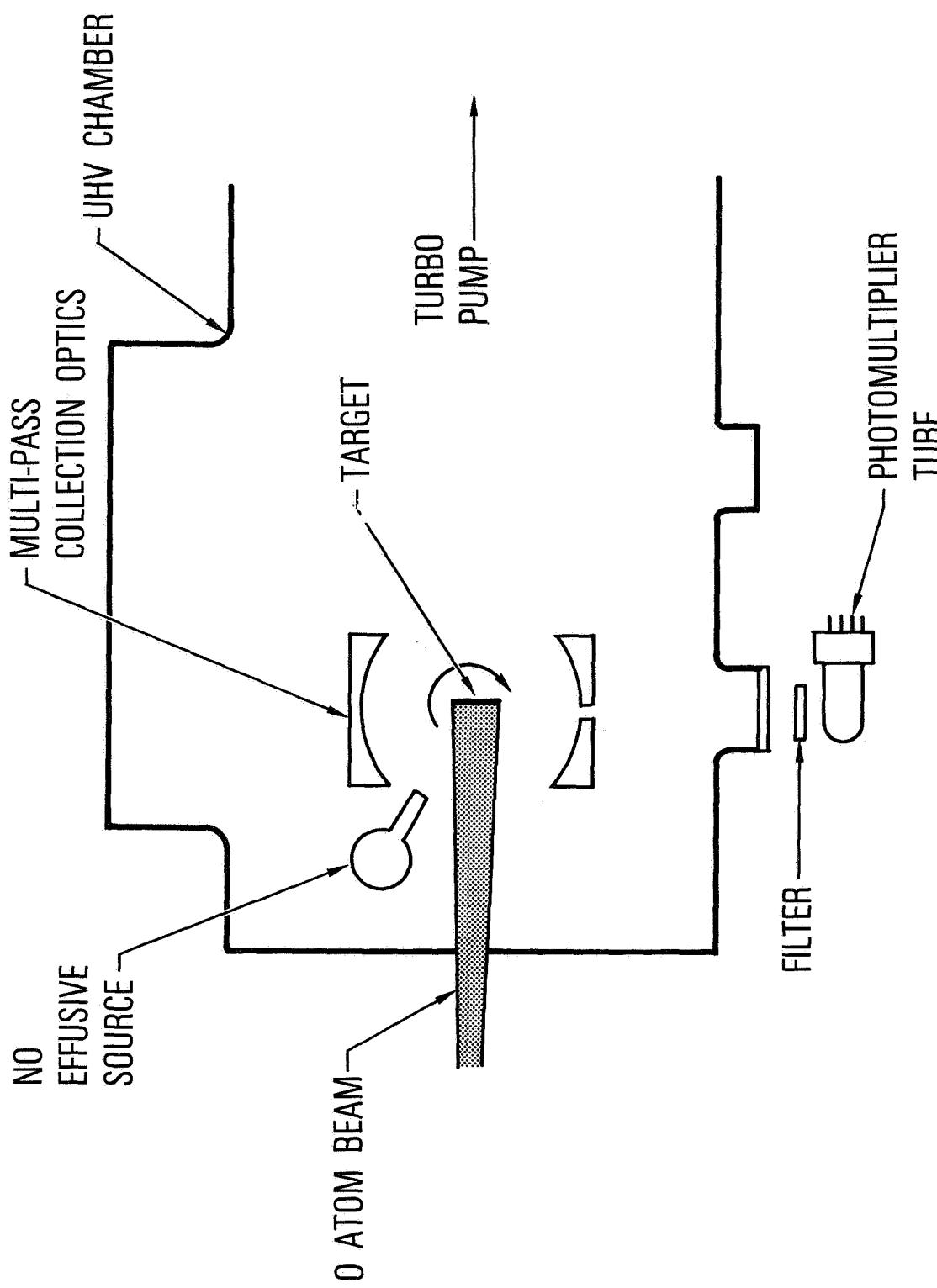


Fig. 4. Schematic representation of a molecular beam surface catalyzed excitation experiment.

TABLE 1. TYPICAL BEAM SOURCE CHARACTERISTICS

Feed Gas	He:O ₂ /98:2
Flow Rate	265 SCFH (2 l-atm sec ⁻¹)
Power Dissipated	16 kW
O Flux on Target ^a	5.0x10 ¹⁵ cm ⁻² sec ⁻¹
O ₂ Flux on Target ^a	7.5x10 ¹⁵ cm ⁻² sec ⁻¹
Beam Velocity (oxygen atoms)	3.5 km sec ⁻¹

^aTarget mounted in chamber 2; see Figure 1.

TABLE 2. COMPARISON OF LABORATORY AND FLIGHT MEASUREMENTS OF THE AVERAGE PROBABILITIES FOR THE REACTION OF ATOMIC OXYGEN WITH KAPTON

Kapton Temperature (kelvin)	Reaction Probability 10 ⁻²⁴ cm ³ /0 atom		
	Laboratory ^a	STS-5 ^b	STS-8 ^c
300	2.1+1.1 1.7+0.9	2.3+0.9	---
338	1.4+0.9	2.0+0.8	3.0+1.2
393	1.5+0.9	2.1+0.9	2.9+1.2

^aArnold and Peplinski [1985b].

^bSee Table 3 of Leger et al. [1983]; Nominal uncertainty is +40%.

^cSee Table 5 of Leger et al. [1984]; Nominal uncertainty is +40%.